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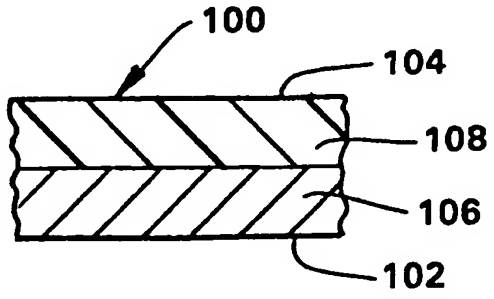
(54) Title: COMPOSITE FOR TRANSFER OF DURABLE GRAPHICS

(57) Abstract

A composite (100) adapted for the transfer of durable graphics having first and second surfaces (102, 104) which includes a first layer (106) defining the first surface and a second layer (108) defining the second surface. The second layer includes a durable thermoplastic polymer in an amount effect to resist the adverse effects of exposure to the weather and an adhesion-promoting thermoplastic polymer in an amount effective to enhance the adhesion of the durable thermoplastic polymer without significantly adversely affecting the extrudability or weatherability of the durable thermoplastic polymer. The durable thermoplastic polymer may include a poly(vinylidene fluoride) and the adhesion-promoting thermoplastic polymer may be a thermoplastic acrylate or methylacrylate polymer or copolymer. The first layer may be a film or a cellulosic nonwoven web.



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COMPOSITE FOR TRANSFER OF DURABLE GRAPHICS

Background of the Invention

The present invention relates to a composite for the transfer of graphics, commonly referred to as a heat transfer material.

Graphics for outdoor use traditionally were created by hand directly on the final surface. The use of heat transfer materials in which graphics are printed on a release or transfer paper and then applied to the final surface by means of heat and pressure (after which the release or transfer paper is removed) is not common, primarily because of deficiencies in the durability of the transferred graphics.

More recently, graphics for outdoor use are created through a two-step process involving the use of computers. First, paint is applied to a suitable flexible substrate, such as paper or a polymeric film, to provide a sheet of a single color. The desired shape, such as a letter or design, then is cut out. The shape is created, and the cutting device guided, by a computer. The shape then is applied to a heavy, scrim-reinforced vinyl by the application of heat and pressure. Other shapes are added as appropriate, in some cases creating a multicolored image consisting of arrays of differently colored shapes. A protective coating then is applied over the final graphic image. The scrim-reinforced vinyl material then is stretched over a metal frame. The frame often is covered on all sides by vinyl and lighted from within. The resulting sign structure is resistant to strong winds, rocks, and debris since it can stretch upon impact and recover.

The protective coating typically is a film of poly(vinyl fluoride), such as Tedlar . While such a film provides excellent protection against the weather, it is expensive. Moreover, the film is relatively hard and does not soften or conform to the irregular surfaces which

inherently result from the process employed. Poly(vinyl fluoride) is not soluble in most solvents and can be applied only as a preformed film. Thus, there is a need for a one-step process which will overcome some of the difficulties associated with the use of an after-applied poly(vinyl fluoride) film.

Summary of the Invention

The present invention addresses some of the difficulties and problems discussed above by providing a composite adapted for the transfer of durable graphics having first and second surfaces which includes a first layer defining the first surface and a second layer defining the second surface. The first layer may be a film or a cellulosic nonwoven web, such as a paper. The second layer includes a durable thermoplastic polymer in an amount effective to resist the adverse effects of exposure to the weather and an adhesion-promoting thermoplastic polymer in an amount effective to enhance the adhesion of the durable thermoplastic polymer without significantly adversely affecting the extrudability or weatherability of the durable thermoplastic polymer. The composite may include a conformable layer interposed between the first layer and the second layer.

By way of example, the durable thermoplastic polymer may include a poly(vinylidene fluoride). The poly(vinylidene fluoride) desirably will be present in an amount of from about 95 to about 50 percent by weight, based on the weight of the second layer.

Also by way of example, the adhesion-promoting thermoplastic polymer may be a thermoplastic acrylate or methacrylate polymer or copolymer. When present, the thermoplastic acrylate or methacrylate polymer or copolymer typically will be present in an amount of from about 5 to about 50 percent by weight, based on the weight of the second layer.

When the first layer is a cellulosic nonwoven web, the composite may include a backsize layer overlaying the second surface of the first layer. Such backsize layer typically will be formed from a dispersion which includes a film-forming latex and an inorganic material, such as clay. A barrier layer may be interposed between the first layer and the second layer. The barrier layer, like the backsize layer, generally will be formed from a dispersion which includes a film-forming latex and an inorganic material. If a conformable layer is employed, it generally will be interposed between the barrier layer and the second layer.

The present invention also provides a composition adapted for the transfer of durable graphics which includes the durable thermoplastic polymer and the adhesion-promoting thermoplastic polymer already described.

Brief Description of the Drawings

FIGS. 1-7 are diagrammatic representations of fragmentary cross-sectional views of various embodiments of the present invention.

Detailed Description of the Invention

The composite of the present invention has a first surface and a second surface. A first layer having a first surface and a second surface defines the first surface and a second layer defines the second surface. The second layer includes a durable thermoplastic polymer in an amount effective to resist the adverse effects of exposure to the weather and an adhesion-promoting thermoplastic polymer in an amount effective to enhance the adhesion of the durable thermoplastic polymer without significantly adversely affecting the extrudability or weatherability of the durable thermoplastic polymer. The foregoing composite is illustrated by FIG. 1, in which there is shown a

diagrammatic representation of a fragmentary cross-sectional view of a composite 100 having a first surface 102 and a second surface 104. The first surface 102 is defined by a first layer 106 and the second surface 104 is defined by a second layer 108.

As used herein, the terms "durable" and "weatherability" have reference primarily to the ability of the second layer to resist the adverse effects of exposure to the weather. The term "durable" also includes such properties as abrasion resistance and resistance to discoloration upon exposure to sunlight.

The durable thermoplastic polymer may include a poly(vinylidene fluoride). The poly(vinylidene fluoride) may be present in an amount of from about 95 to about 50 percent by weight, based on the weight of the second layer. As used herein, the terms "poly(vinylidene fluoride)" and "vinylidene fluoride polymer" are meant to include homopolymers of vinylidene fluoride and copolymers of vinylidene fluoride and minor amounts, i.e., less than about 30 percent by weight, of one or more other unsaturated monomers. Such other unsaturated monomers desirably will be fluorinated or perfluorinated unsaturated monomers. The term also is meant to include a single poly(vinylidene fluoride) and a blend of two or more different vinylidene fluoride polymers.

The adhesion-promoting thermoplastic polymer may be a thermoplastic acrylate or methacrylate polymer or copolymer. Thus, the adhesion-promoting thermoplastic polymer may be a polyacrylate or a polymethacrylate. Alternatively, the adhesion-promoting thermoplastic polymer may be an alternating, random, or block copolymer of two or more unsaturated monomers, provided that at least about 50 percent by weight of such monomers are acrylate and/or methacrylate monomers. Examples of acrylate and methacrylate monomers include, by way of illustration only, methyl acrylate, methyl methacry-

late, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, t-butyl acrylate, and the like.

When employed, the thermoplastic acrylate or methacrylate polymer or copolymer may be present in an amount of from about 5 to about 50 percent by weight, based on the weight of the second layer. Desirably, the thermoplastic acrylate or methacrylate polymer or copolymer will be present in an amount of from about 20 to about 30 percent by weight.

From the foregoing, it is clear that the second layer is formed from a composition which includes the durable thermoplastic polymer and adhesion-promoting thermoplastic polymer described above. Such composition also may include other components, provided they do not significantly adversely interfere with the durability and adhesion of the layer formed therefrom. Such other components include, by way of illustration only, melt viscosity modifiers, antioxidants, ultraviolet radiation absorbers, and the like.

The composite of the present invention also may include a conformable layer interposed between the first layer and the second layer, as shown in FIG. 2. In FIG. 2, a diagrammatic representation of a fragmentary cross-sectional view of a composite 200 is shown. The composite 200 has a first surface 202 and a second surface 204. The first surface 202 is defined by a first layer 206 and the second surface 204 is defined by a second layer 208. Interposed between the first layer 206 and the second layer 208 is a conformable layer 210. The conformable layer may include copolymers of ethylene and vinyl acetate or copolymers of ethylene and acrylic acid. Both types of copolymers generally will have melt indices greater than about 30. The melt index is determined in accordance with ASTM Standard Method D1238-82, note 16. For example, the conformable layer may be composed of a wax-modified ethylene/vinyl acetate copolymer sold under the trade designation Elvax 3200 (E. I. DuPont de Nemours &

Co., Inc., Wilmington, Delaware). The conformable layer may be applied as a hot melt or an extruded film, typically at a thickness of from about 0.4 to about 3 mils (from about 0.01 mm to about 0.08 mm). Because of the nature of the conformable layer and its rheology, it will, when heated, allow the composite to contact uneven surfaces.

The first layer in general may be any material suitable for the intended purpose. The first layer typically will be a flexible sheet material, such as a film or a cellulosic nonwoven web, e.g., a paper. When the first layer is a cellulosic nonwoven web, such as a paper, a backsize layer may overlay the first surface, i.e., the second surface of the first layer, as shown in FIG. 3 which is a diagrammatic representation of a fragmentary cross-sectional view of a composite 300. The composite 300 has a first surface 302 and a second surface 304. The first surface 302 is defined by a first layer 306 having a first surface 308 and a second surface 310. The second surface 304 is defined by a second layer 312. Overlaying the second surface 310 of the first layer 306 is a backsize layer 314.

The backsize layer generally is prepared from a binder and clay. For example, the binder may Rhoplex HA-16 (Rohm and Haas Company, Philadelphia, Pennsylvania), a polyacrylate. The clay may be Ultrawhite 90 (Englehard, Charlotte, North Carolina). In a typical preparation, the two materials are mixed in amounts which will provide roughly 70-80 percent by weight on a dry weight basis of the clay. Water and/or a thickening agent are added as necessary to give a final dispersion viscosity in the range of 0.100-0.140 Pa s (100-140 centipoise) at ambient temperature. However, lower amounts of clay may be employed, if desired, or the clay may be omitted entirely.

The composite of the present invention also may include a barrier layer. In general, the barrier layer may be interposed between the first layer and the second layer. The barrier layer, like the backsize layer, generally will be formed from a dispersion which includes a film-

forming latex and an inorganic material. If both a barrier layer and a conformable layer are employed, the latter generally will be interposed between the barrier layer and the second layer. The use of a barrier layer and/or a conformable layer may be in conjunction with the use of a backsize layer as already described. These variations are illustrated by FIGS. 4-7, each of which is a diagrammatic representation of a fragmentary cross-sectional view of a composite of the present invention.

FIG. 4 shows a composite 400 having a first surface 402 and a second surface 404. The first surface 402 is defined by a first layer 406 and the second surface 404 is defined by a second layer 408. Interposed between the first layer 406 and the second layer 408 is a barrier layer 410. In FIG. 5, there is shown a composite 500 having a first surface 502 and a second surface 504. The first surface 502 is defined by a first layer 506 having a first surface 508 and a second surface 510. The second surface 504 is defined by a second layer 512. Overlaying the second surface 510 of the first layer 506 is a backsize layer 514. Interposed between the first layer 506 and the second layer 508 is a barrier layer 516.

Turning now to FIG. 6, there is shown a composite 600 having a first surface 602 and a second surface 604. The first surface 602 is defined by a first layer 606 having a first surface 608 and a second surface 610. The second surface 604 is defined by a second layer 612. Overlaying the second surface 610 of the first layer 606 is a backsize layer 614. Interposed between the first layer 606 and the second layer 612 is a conformable layer 616. Finally, FIG. 7 shows a composite 700 having a first surface 702 and a second surface 704. The first surface 702 is defined by a first layer 706 having a first surface 708 and a second surface 710. The second surface 704 is defined by a second layer 712. Overlaying the second surface 710 of the first layer 706 is a backsize layer 714. Overlaying the first surface

708 of the first layer 706 is a barrier layer 716. Interposed between the first layer 706 and the barrier layer 716 is a conformable layer 718.

As with the backsize layer, the barrier layer also generally is prepared from a binder and clay. For example, a dispersion may be used which consists of, on a dry weight basis, 100 parts of Styronal 4574, a styrene-butadiene rubber (BASF, Sarnia, Ontario, Canada), 57.5 parts of Hycar 2600x106, an acrylic polymer (B. F. Goodrich Company, Cleveland, Ohio), and 30 parts of a clay, such as Ultra-white 90. Alternatively, the barrier layer may be prepared from a mixture of Michem Prime 4983, an ethylene-acrylate copolymer (Michelman, Inc. Cincinnati, Ohio), and Ultrawhite 90 clay in a ratio of 25 parts to 100 parts, respectively, on a dry weight basis. The barrier coating latex may be applied with a Meyer rod to provide a coating basis weight of, by way of illustration, 14-17 gsm.

The composite of the present invention is prepared by methods which are well known to those having ordinary skill in the art. In general, the second layer typically is formed on the first layer by melt extrusion of a mixture of the durable thermoplastic polymer and the adhesion-enhancing thermoplastic polymer. Melt extrusion also is employed to form the conformable layer on the appropriate layer or surface. The backsize and barrier layers usually are formed by the application of an dispersion, such as one or more of those already noted. Application can be by Meyer rod, doctor blade, or other suitable method.

The composite of the present invention may be used in a variety of ways for the transfer of graphics. For example, graphics may be printed on the second surface with inks or paints which also act as adhesives on the application of heat and pressure. The printed second surface then is overlaid with a heavy vinyl material and the combination placed in a heated press. Removal of the composite results in the transfer to the vinyl of the graphics and the second layer

which serves to protect the graphics in an outdoor environment. The vinyl material then may be stretched over a metal frame as described earlier. As another example, the second surface may be coated with a clear adhesive, placed against an already prepared sign or other graphic structure, and subjected to heat and pressure in the usual manner. Removal of the composite results in the transfer to the sign or other graphic structure of the second layer which serves to protect the graphics already in place on the sign or other graphic structure.

The present invention is further described by the example which follows. Such example, however, is not to be construed as limiting in any way either the spirit or the scope of the present invention.

Example

This example describes the preparation of a composite of the present invention, as illustrated by FIG. 7. The first layer 706 was a latex-impregnated paper prepared from softwood kraft fibers. The basis weight of the paper was 52 grams per square meter (gsm) and the paper had an eight-sheet Gurley porosity of 10 seconds per 100 cubic centimeters of air. The saturant was a poly(ethyl acrylate) latex (Hycar 26083, B. F. Goodrich Company, Cleveland, Ohio). Saturant add-on was 28 parts of latex per 100 parts of fiber on a dry weight basis. The saturant also contained small amounts of defoamer, antioxidants, and surfactants.

To one side (i.e., the second surface 710) of the paper was applied a backsize coating or layer 714 consisting of a mixture of Rhoplex HA-16 and Ultrawhite 90 clay in a ratio of 26 parts to 100 parts, respectively, on a dry weight basis. The coating dispersion was diluted with water to a solids content of 62 percent by weight and applied to the paper with a Meyer rod. The dry coating basis weight was 22 gsm.

The other side (i.e., the first surface 708) of the paper was coated with a barrier layer 716 consisting of Michem Prime 4983 and Ultrawhite 90 clay in a ratio of 25 parts to 100 parts, respectively, on a dry weight basis. The basis weight of the barrier layer was 14 gsm.

The barrier layer 716 in turn was coated with a conformable layer 718 which consisted of coextruded Elvax 3180, an ethylene-vinyl acetate copolymer containing 25 percent by weight of vinyl acetate and reported to have a melt index of 30 g/10 minutes (E. I. DuPont de Nemours & Co., Inc., Wilmington, Delaware), and Surlyn 1702 ionomer (DuPont). The Elvax 3180 layer was adjacent to the barrier layer and was 1.2 mils (about 0.03 mm) thick; the Surlyn 1702 layer was 0.4 mil (about 0.01 mm) thick.

The second layer 712 consisted of a blend of Kynar Flex 2800, Acryloid B-44, and Cyasorb UV 5411, a light stabilizer and ultraviolet radiation absorber (American Cyanamide, Wayne, New Jersey). Each 100 parts of coating contained 74.5 parts, 25 parts, and 0.5 parts by weight, respectively, of the three ingredients. Kynar Flex 2800 (Atochem North America, Philadelphia, Pennsylvania) is a vinylidene fluoride-hexafluoropropylene copolymer in which the amount of hexafluoropropylene is about 10 percent by weight. Acryloid B-44 (Rohm and Haas Company, Philadelphia, Pennsylvania) is a polyacrylate resin designed primarily for industrial finishing. The ingredients were combined dry, blended, then extruded at a melt temperature of 249°C through a slot die onto the Surlyn 1702 side of the conformable layer 718. A high-gloss chill roll was used. The thickness of the layer was 1.1 mils (about 0.03 mm).

The peel strength of the conformable and second layers was estimated to be of the order of 130-140 grams per inch (about 51-55 grams per cm) at a 180° angle using a one-inch (about 2.5-cm) strip. This is sufficient peel strength to allow coating the composite with inks or graphics, but low enough to allow removal of the first and associated layers (i.e., barrier layer 716, first layer 706, and backsize layer 714) after transfer to, for example, a sign face. The second layer side of the composite was very soft, yet tough.

While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

WHAT IS CLAIMED IS:

1. A composite adapted for the transfer of durable graphics having first and second surfaces comprising:

a first layer defining the first surface; and

a second layer defining the second surface, which layer comprises

a durable thermoplastic polymer in an amount effective to resist the adverse effects of exposure to the weather; and

an adhesion-promoting thermoplastic polymer in an amount effective to enhance the adhesion of the durable thermoplastic polymer without significantly adversely affecting the extrudability or weatherability of the durable thermoplastic polymer.

2. The composite of claim 1, in which the durable thermoplastic polymer comprises a poly(vinylidene fluoride).

3. The composite of claim 2, in which the poly(vinylidene fluoride) is present in an amount of from about 95 to about 50 percent by weight, based on the weight of the second layer.

4. The composite of claim 2, in which the adhesion-promoting thermoplastic polymer is a thermoplastic acrylate or methacrylate polymer or copolymer.

5. The composite of claim 3, in which the adhesion-promoting thermoplastic polymer is a thermoplastic acrylate or methacrylate polymer or copolymer.

6. The composite of claim 5, in which the thermoplastic acrylate or methacrylate polymer or copolymer is present in an amount

of from about 5 to about 50 percent by weight, based on the weight of the second layer.

7. The composite of claim 1, in which the first layer is a film.

8. The composite of claim 1, in which the first layer is a cellulosic nonwoven web.

9. The composite of claim 8, in which the first layer is a paper.

10. A composite adapted for the transfer of durable graphics which comprises:

a first layer having first and second surfaces and selected from the group consisting of films and cellulosic nonwoven webs; and

a second layer overlaying the first surface of the first layer which comprises:

a durable thermoplastic poly(vinylidene fluoride) in an amount effective to resist the adverse effects of exposure to the weather; and

an adhesion-promoting thermoplastic polymer in an amount effective to enhance the adhesion of the durable thermoplastic polymer without significantly adversely affecting the extrudability or weatherability of the durable thermoplastic polymer.

11. The composite of claim 10, in which the poly(vinylidene fluoride) is present in an amount of from about 95 to about 50 percent by weight, based on the weight of the second layer.

12. The composite of claim 10, in which the adhesion-promoting thermoplastic polymer is a thermoplastic acrylate or methacrylate polymer or copolymer.

13. The composite of claim 11, in which the adhesion-promoting thermoplastic polymer is a thermoplastic acrylate or methacrylate polymer or copolymer.

14. The composite of claim 13, in which the thermoplastic acrylate or methacrylate polymer or copolymer is present in an amount of from about 5 to about 50 percent by weight, based on the weight of the second layer.

15. The composite of claim 10, in which a conformable layer is interposed between the first layer and the second layer.

16. The composite of claim 10, in which the first layer is a cellulosic nonwoven web.

17. The composite of claim 16, in which the composite further comprises a first barrier layer overlaying the second surface of the first layer.

18. The composite of claim 16, in which a second barrier layer is interposed between the first layer and the second layer.

19. The composite of claim 18, in which a conformable layer is interposed between the second barrier layer and the second layer.

20. A composition adapted for the transfer of durable graphics comprising:

a durable thermoplastic polymer; and

an adhesion-promoting thermoplastic polymer.

21. The composition of claim 20, in which the durable thermoplastic polymer comprises a poly(vinylidene fluoride).

22. The composition of claim 21, in which the poly(vinylidene fluoride) is present in an amount of from about 95 to about 50 percent by weight, based on the weight of the composition.

23. The composition of claim 21, in which the adhesion-promoting thermoplastic polymer is a thermoplastic acrylate or methacrylate polymer or copolymer.

24. The composition of claim 23, in which the thermoplastic acrylate or methacrylate polymer or copolymer is present in an amount of from about 5 to about 50 percent by weight, based on the weight of the composition.

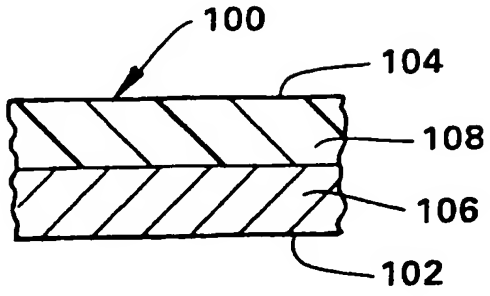

FIG. 1

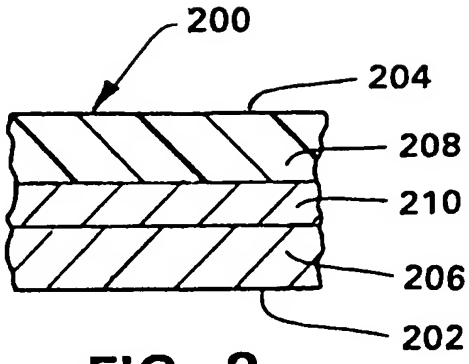

FIG. 2

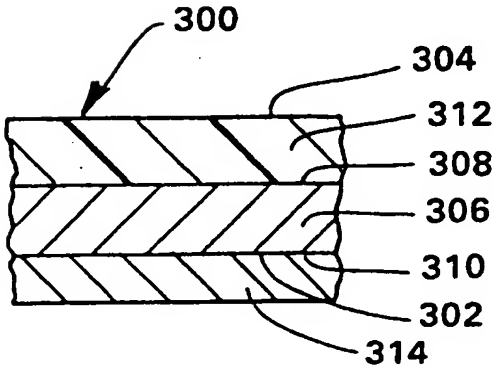

FIG. 3

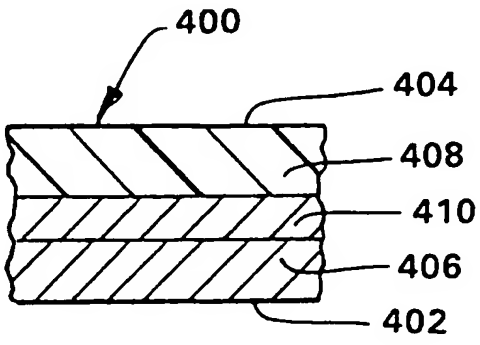

FIG. 4

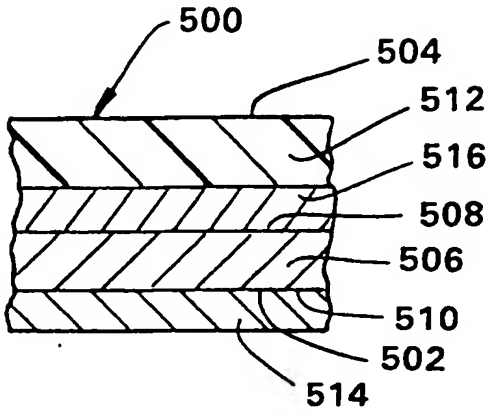

FIG. 5

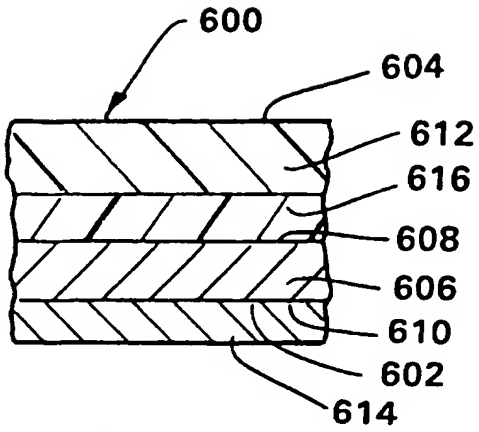

FIG. 6

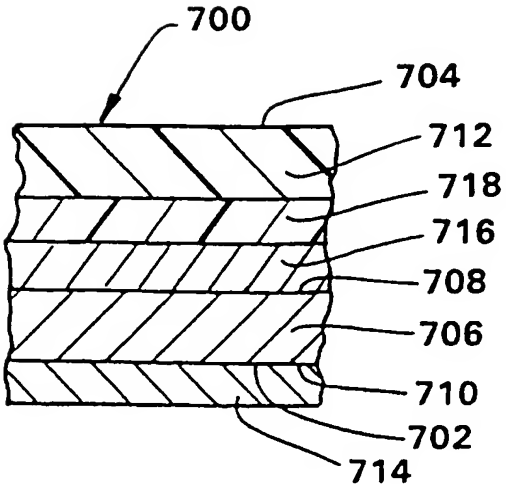

FIG. 7

INTERNATIONAL SEARCH REPORT

Interr al Application No
PCT/US 95/10176

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B44C1/165 B44C1/17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B44C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9347 Derwent Publications Ltd., London, GB; Class A32, AN 93-374153 & JP,A,05 278 137 (TOPPAN PRINTING CO LTD) , 26 October 1993 see abstract ---	1,2,4,7, 10
X	PATENT ABSTRACTS OF JAPAN vol. 016 no. 284 (M-1270) ,24 June 1992 & JP,A,04 073183 (DAINIPPON PRINTING CO LTD) 9 March 1992, see abstract	1,8,9
A	--- -/--	2,4

[X] Further documents are listed in the continuation of box C.

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9 November 1995	08.12.95

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INTERNATIONAL SEARCH REPORT

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